

THE USE OF FLY ASH AS A POZZOLANIC MATERIAL IN
PORTLAND CEMENT CONCRETE

by

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INTRODUCTION

General

Pozzolans are usually defined as siliceous or siliceous and aluminous materials, which in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. This calcium hydroxide is usually the product of hydration of Portland cement.

Pozzolans could be divided into two groups as follows:

1. The natural pozzolans, which are for the most part materials of volcanic origin, include also certain diatomaceous earths which are composed of the siliceous skeletons of diatoms deposited from either fresh or sea water.

2. The artificial pozzolans which are mainly products obtained by the heat treatment of natural materials such as clay and shales and some siliceous rocks and pulverized fuel ash (fly ash).

Although this research has been conducted entirely on fly ash, the author studied a great deal on several kinds of pozzolanic materials. To acquire a general knowledge of the natural pozzolans, as well as the artificial pozzolans, is particularly important for the author whose home country is the Arab World which contains mainly natural pozzolans rather than artificial pozzolans.

It is a fact that natural volcanic ash deposits that are fit for use as pozzolans are numerous in the United States of America and many other parts of the world such as Italy. The use of such materials as pozzolanic cements has been followed for a long time. In fact, it is interesting to know that such volcanic materials have been used as pozzolanic cements in mortars in Italy and along the Rhine since the old Roman Empire about 2,000 years ago. In Italy pozzolanic volcanic ash was used to build the big storm-water pipes and conduits.

Not all volcanic ashes possess pozzolanic properties since some are suitable only for use as inert sands. This pertains to the fact that the pozzolanic character of a material depends not only on its volcanic origin but also on the eruptive conditions of its formation.

Types of Natural Pozzolans

Volcanic Tuffs. The pozzolans of volcanic origin consist of tuffs arising from the deposition of volcanic dust and ash. They may occur in a consolidated rock-like form underlying material deposited subsequently like the Rhenish Trass, or in a more fragmentary or unconsolidated state like some of the Italian pozzolans which are the most exploited pozzolans in Europe until now.

The tuff pozzolans are composed of a mixture of silicates and contain both glass and crystalline particles. They were formed from volcanic ash as a result of rapid cooling and in some the super-heated steam and carbon dioxide below the earth's surface produced considerable chemical alterations which converted

much of the original materials into a more chemically reactive form. The active part of pozzolans is the amorphous portion and to a lesser extent the partially altered minerals. Very little activity can be attributed to the crystalline components for these are well defined stable compounds inert to lime.

There is no relation between the content of combined water in tuffs and their hydraulic properties. This also applies to the other volcanic pozzolans.

Three theories have been advanced to explain the reason for the activity of the non-crystalline material in volcanic ashes.

1. In the first theory the non-crystalline material is considered to be an active alteration product of the original minerals, produced by prolonged exposure, after deposition, to waters containing carbon dioxide and to superheated steam.

2. In the second theory the pozzolans are considered to originate from materials carried by volcanic eruption from geological strata of essentially clay-like composition and have undergone, during eruption, heating sufficient to produce complete dehydration and chemical alteration, but not fusion. This theory neglects the alterations that occur in the chemical characteristics of the volcanic ashes after deposition.

3. In the third theory the pozzolanic activity is attributed primarily to the physical state of the material caused only by the eruptive condition with neglect to subsequent alterations. Since the amorphous portion of pozzolans is essentially a very porous aerogel of high internal surface area, the pozzolanic activity has been attributed to this high surface area.

The effect of heating on natural volcanic pozzolans is variable. At temperatures of 500° C. to 600° C. the material may be dehydrated without any collapse of the atomic or physical structure on which their activity depends, but at red heat the activity is much decreased or lost. From this it could often be concluded that the effect of heat treatment is to calcine any clay constituents to inert or pozzolanic ones.

Diatomaceous Earths. They are composed of siliceous skeletons of diatoms deposited from either fresh or sea-water. In many cases the deposits are mixed with sand and clay. The largest known deposits are those in California. Other large deposits are found in Algeria, Canada, Denmark and Germany. Diatomaceous earths require plenty of water when used as pozzolans.

Types of Artificial Pozzolans

The chief artificial pozzolans are burnt clays and shales, spent oil, burnt gaise, burnt moler, si-stoff, bauxite, granulated blast furnace slag and pulverized fuel ash (or fly ash). A brief description of each will be given except for the fly ash which will be discussed in detail.

Burnt Clay and Shales. Burnt clay pozzolans are produced by burning suitable clays or shales at a temperature which varies from 600° C. to over 900° C., depending on the nature of the clay and the conditions of burning. The product is ground to cement fineness.

The pozzolanic properties of burnt clays were well known to the Romans who utilized ground clay bricks and tiles as a sub-

stitute for the natural volcanic ash pozzolans. Also Egypt and India have known the pozzolanic value of burnt clays which are called "Homra" in Egypt and "Surkhi" in India. In Egypt lime-burnt clay mortar was used initially for the hearting to the nowadays controversially famous Assuan Dam and found to yield a more watertight mortar than a 1:4 Portland cement-sand mix. Its use was, however, given up owing to difficulties in producing the material at the required rate. The slow rate of setting of the material also hindered the progress of construction. A clearly observed sight all over Asia is the corrugated burnt clay tile roofing of buildings.

Raw clays consist essentially of a group of hydrated aluminum silicates. All clays have a considerable content (10-15%), of combined water and the changes that clays undergo when this water is lost are not known exactly. Probably a mixture of amorphous silica and alumina is formed.

Burnt Gaise. Gaise is a soft, porous, highly siliceous sedimentary rock containing a proportion of clay. It is found in France and used either in the raw state or burnt at 900° F.

Moler. The burnt moler is better than the raw moler. It is used with Portland cement for work in sea-water.

Si-Stoff. Si-Stoff is a siliceous waste product obtained in the manufacture of alum which was used to some extent in Germany as a pozzolan. Though sometimes si-stoff possesses good pozzolanic activity, it suffers from the disadvantages of waste products which are variability in composition and suitability for use. It also contains high percentages of sulfur trioxide (SO_3).

Pulverized Fuel Ash (Fly Ash). When pulverized coal is burnt in boilers the ashes are carried forward in the gases as fused particles which solidify into a roughly spherical shape. This powdery residue is collected, in modern power plants, at the entrance of the stack by electrical or mechanical precipitators in order to prevent pollution of the air. In the last decade or two laws were enacted in mostly every industrial city requiring the filtration of the gases coming out of the chimneys of factories burning coal. This requirement created a new problem for the factory. This problem was not the filtration itself but the way to dispose of the fly ash filtered. It is interesting to sight an example indicating the importance of such a problem. One power plant in Chicago, Illinois, used a former swampy land as a dump area for the fly ash collected. This land was of an appreciable depth before being used as a dump but was filled and elevated well above adjacent ground in a period of about four years. No other dumps were available and the disposal of fly ash became very expensive. Such problems of disposal lead to investigations for new methods of disposal until it was discovered that most of the fly ashes possess pozzolanic properties. This meant the possibility of their use as additives to concrete mixes. Continued investigations proved the possibility of the use of fly ashes as substitutes for a portion of the Portland cement required in a concrete mix instead of being mere additives.

[Fly ash is usually finer than Portland cement and consists mostly of small spheres of glassy compounds of complex chemical composition together with miscellaneous materials such as quartz,

feldspar, iron oxides and carbon. Combustible matter is always present in fly ash, but in well burnt material it is below ten percent although it might drop to one percent or two percent or rise to 20 percent or 30 percent differing with different power stations. Most of the fly ashes possess pozzolanic properties although some do not. The specific gravity varies from below 2.00 to above 2.60 and tends to be lower as the carbon content rises.

During recent years there has been a growing interest of the governmental and industrial organizations in the use of fly ash in concrete. Research reports indicating the beneficial use of fly ash and the resulting good qualities of concrete such as better workability and decreased bleeding of the plastic concrete motivated such interest. It was found that the segregation of the aggregates in concrete was decreased. Also less rise in temperature in hardening concrete, less permeability, better resistance to sulfate attack and reduced expansion resulting from the reaction between the alkalies of the cement and certain types of aggregate were some of the benefits produced by the use of fly ash in concrete thus promoting such use. All these advantages lead to the widespread research on fly ash and to the subsequent use of it although not on a wide scale yet because of the many unanswered questions about its behavior in concrete under actual use.

Although the Bureau of Reclamation has set some specifications about the moisture content, loss on ignition, and permeability of the acceptable fly ashes for use in concrete, no adequate specifications are available for fly ash. Even the A. S. T. M. (American

Society of Testing Materials) specifications for the methods of testing are believed to be unsatisfactory.

This research was conducted by Kansas State College primarily to study the pozzolanic behavior of fly ash as shown by its effect on Portland cement-fly ash mortars. The results when reported to the Chicago Fly Ash Company and to the extension cooperative program committee are to help in the production of better fly ashes by controlling the burning process and to attempt to establish some acceptable specifications for the use of fly ash as a substitute for a portion of the cement in concrete, and for the selection of the suitable fly ashes to be used as such. The strengths developed in mortars containing fly ash were used to study the relations between pozzolanic activity and the various chemical and physical properties of fly ash. A study was also made of the effectiveness of fly ash in reducing expansion due to alkali-aggregate reaction. All this shall be discussed in details in the following pages.

CHEMICAL AND PHYSICAL PROPERTIES OF FLY ASH

The results of chemical analysis showing the principal constituents of some of the samples of fly ashes used in this research are given in Table 1. In this table the fly ashes are arranged in descending order according to their contents of sulfur trioxide (SO_3). It is obvious that the Ridgeland (symbolized by the letter R) fly ash supplied by the Chicago Fly Ash Company contains the highest amount (14.68%) of sulfur trioxide (SO_3) while the new Stateline (symbolized by Sn) fly ash has the lowest content (1.02%)

of sulfur trioxide (SO_3). Since the main interest of this research was to determine the best fly ash with the appropriate quantity of sulfur trioxide, most of the discussion will be concentrated around the effects of different percentages of sulfur trioxide on the properties of the mortar such as strength and expansion and contraction.

Although the carbon content is not reported in the table the carbon could be calculated easily as follows:

Taking the new Stateline fly ash (Sn) one finds the following data in Table 1.

Sulfur Trioxide	= 1.02%
Moisture	= 0.27%
Loss on ignition @ 750° C.	= 1.51%
SO_3 left after ignition at 750° C.	= 0.98%
Loss on ignition at 950° C.	= 2.52%
SO_3 left after ignition at 950° C.	= 0.33%
SO_3 lost on ignition at 750° C.	= 1.02 - 0.98
	= 0.04%
(SO_3 + Moisture)	= 0.27 + 0.04
	= 0.31%
Carbon burned at 750° C.	= 1.51 - 0.31
	= 1.20%
<hr/>	
SO_3 lost on ignition at 950° C.	= 1.02 - 0.33
	= 0.69%
(SO_3 + Moisture)	= 0.69 + 0.27
	= 0.96%

Table 1. Chemical analysis of fly ashes used.

Components	: Ridge- : land		: BLR3- : H5		: North- : western		: Fisk : State- : F : line		: Paddy's : State- : Run : line	
	: R	: %	: B	: %	: W	: %	: %	: S	: X	: Sn
According to A.S.T.M., C113 and C114										
Sulfur Trioxide SO ₃	14.68		9.02		4.09		4.08	3.24	1.58	1.02
Silicon Dioxide SiO ₂	36.60		40.45		40.07		43.56	45.83	40.60	47.06
Aluminum Oxide Al ₂ O ₃	16.06		17.28		20.55		19.13	19.96	19.41	22.51
Ferric Oxide Fe ₂ O ₃	16.30		16.50		18.58		16.45	17.02	22.90	18.82
Calcium Oxide CaO	5.37		4.32		2.15		7.28	6.68	4.48	3.24
Magnesium Oxide MgO	0.98		0.87		1.18		1.64	1.30	0.59	0.22
Loss on ignition	6.76		4.51		1.57		1.00	1.05	6.31	1.51
Moisture	1.20		0.73		0.47		0.32	0.38	0.31	0.27
Potassium Oxide K ₂ O	3.46		3.35		1.96		2.01	2.13	1.92	2.16
Sodium Oxide Na ₂ O	2.72		2.79		3.47		2.85	2.37	0.69	0.95
Water Soluble K ₂ O										
Water (A.S.T.M. C114)	0.96		0.63		0.05		0.07	0.09	0.03	0.04
Water Soluble Na ₂ O										
Water (A.S.T.M. C114)	2.04		1.62		0.69		0.53	0.37	0.02	0.05
Water Soluble SO ₃	12.37		7.96		2.04		1.94	1.74	0.61	0.52
Loss on ignition at 950°C.										
(A.S.T.M. C114)	11.24		12.16		1.96		1.67	1.63	8.21	2.52
SO ₃ remaining after ignition at 950°C.	6.26		0.31		-		-	-	0.15	0.33
SO ₃ remaining after ignition at 750°C.	9.53		-		-		-	-	1.44	0.98
Fineness (By No. 200 sieve)	96.48		97.40		97.04		98.68	97.90	95.10	93.00

Carbon burned at 950° C.

= 2.52 - 0.96

= 1.56%

The two amounts of carbon calculated above indicate that the largest amount of carbon is present as a compound of some sort such as calcium carbonate which is decomposed by heating. The presence of calcium hydroxide will cause a change in the amounts calculated above because by decomposing at these high temperatures it gives off water vapor during the heating. This water vapor is, however, included in the carbon calculated above. Therefore, the difference between the amounts of carbon burned at 950° C. and 750° C. could be attributed to the presence of some calcium hydroxide and or some calcium carbonate.

The finenesses as calculated by the No. 200 sieve in accordance with the A. S. T. M., C184-44, Specification for Hydraulic Cement Fineness, were either equal to or greater than those of the cements. The Lehigh cement used had a fineness of 97.66 percent passing the No. 200 sieve while the Penn Dixie had 97.72 percent passing the No. 200 sieve. These values as compared with the values in Table 1 show that the finenesses were close to one another and that the Fisk with 4.08 percent SO₃ and the Stateline with 3.24 percent SO₃ had the highest finenesses.

An X-ray diffraction analysis of the Ridgeland fly ash (with the highest SO₃ content) was conducted by the Halliburton Research and Testing Laboratories of Duncan, Oklahoma. This test showed that part of the sulfur was present as calcium sulfate (anhydrite). No indications of other sulfates were present although small

amounts below the limits of detection of the test could have been present. Examination of the water-soluble material according to this test proved the presence of hydrated calcium sulfate (gypsum). Anhydrous calcium sulfate and a small amount of iron oxide (Fe_2O_3) were obtained by ignition of the water-soluble material at moderate temperatures.

Water extraction of this Ridgeland fly ash converted the anhydrite to gypsum (hydrated calcium sulfate), but the residue from the evaporation of the water extract did not show any evidence of the presence of other soluble sulfates. It is interesting to note that the water extract was quite acidic, whereas, with ordinary fly ashes, the water extract is usually quite basic. This acidity could be attributed to the large quantity (14.68%) of sulfur trioxide in this particular fly ash.

Heavy-metal analysis by X-ray fluorescence methods showed that iron, a small amount of zinc, and trace of arsenic, titanium and vanadium were present in the Ridgeland fly ash.

CHEMICAL AND PHYSICAL PROPERTIES OF THE CEMENTS USED

As defined by the A. S. T. M. Standards of 1955, Portland cement is the product obtained by pulverizing clinker consisting essentially of hydraulic calcium silicates, to which no additions have been made subsequent to calcination other than water and/or untreated calcium sulfate, except that additions not to exceed 1.0 percent of other materials may be interground with the clinker at the option of the manufacturer, provided such materials in the

amounts indicated have been shown to be not harmful by tests carried out or reviewed by special Committee C-1 on cement.

The A. S. T. M. standards specify five types of cement:

Type I: For general use.

Type II: For use in general concrete construction exposed to moderate sulfate action, or where moderate heat of hydration is required.

Type III: For use when high early strength is required.

Type IV: For use when a low heat of hydration is required.

Type V: For use when high sulfate resistance is required.

The following cements were used in this research:

1. Lehigh (Lh) - A low tricalcium aluminate (C_3A) cement of low alkali as Na_2O equivalent and is either Type I or II cement. This cement contains 1.54 percent sulfur trioxide.

2. Penn Dixie (PD) - A high tricalcium aluminate (C_3A) cement of low alkali as Na_2O equivalent and is Type I cement. Two different batches of this cement were obtained at different periods and were designated as (PD) and (PDn). The sulfur trioxide contents were 1.76 percent for (PD) and 1.79 percent for (PDn). Both batches (PD) and (PDn) are very close to one another in their chemical components. The high percentage of loss on ignition reported for the Lehigh (Lh) and the Penn Dixie (PD) are due to bad storage during usage and before being analyzed which enabled the cements to absorb moisture from the air.

3. Universal Atlas (UA) - A high tricalcium aluminate (C_3A) cement of high alkali as Na_2O equivalent and is Type I cement. It contains 1.90 percent sulfur trioxide.

4. Lone Star (LS) - A Type III cement of high sulfur trioxide content.

The results of chemical analysis showing the principal constituents of some of the cements used in this research together with some physical properties such as fineness are given in Table 2. From this table it is clear that the sulfur trioxide of the cement never exceeded the three percent.

The quantity of calcium hydroxide liberated through the hydration of Portland cement is dependent upon the composition of the cement, being greater for cements which are high in tricalcium silicate (C_3S) than for those which are low in tricalcium silicate. Therefore, Type I and Type II cements produce less calcium hydroxide than Type III. Thus the properties of the mortar or concrete made of Type I or Type II cements do not improve as much as those made of Type III cement by the use of pozzolans because they do not produce the calcium hydroxide necessary for the chemical combination with the pozzolans in large enough quantities.

A STUDY OF THE EFFECTS OF " SO_3 " IN FLY ASH AND CEMENT
AND THE SUITABLE LIMITS FOR " SO_3 " IN FLY ASH

Compressive Strength

The test specimens for determining the effect of fly ash on the compressive strength of mortar were two-inch cubes, and were made both from a control mortar containing no fly ash and test mortars in which 25 percent by weight of the cement were replaced by an equal volume of fly ash. This percentage was taken from previous research conducted on fly ash by previous Kansas State

Table 2. Chemical analysis and some physical properties of some of the cements used.

Components	Lehigh : Lh : %	Penn Dixie : PD : %	Penn Dixie (new) : PDn : %	Universal Atlas : UA : %
<u>Compound composition</u>				
Tricalcium silicate C_3S	47.5	52.3	51.3	44.0
Tricalcium aluminate C_3A	5.9	10.0	12.0	14.1
Dicalcium silicate C_2S	29.1	23.3	24.9	26.5
Tetracalcium aluminum ferrite C_4AF	-	-	6.6	7.6
<u>Chemical analysis</u>				
Sulfur trioxide SO_3	1.54	1.76	1.79	1.90
Loss on ignition	4.14	3.10	1.04	0.76
Silicon dioxide SiO_2	22.62	21.86	22.16	30.80
Aluminum oxide Al_2O_3	4.11	5.33	5.92	6.90
Ferric oxide Fe_2O_3	2.93	2.41	2.16	2.50
Calcium oxide CaO	62.80	64.53	65.78	63.30
Magnesium oxide MgO	1.47	0.79	0.89	2.60
Sodium oxide Na_2O	0.19	None	0.02	0.36
Potassium oxide K_2O	0.25	0.10	0.15	0.76
<u>Fineness</u>				
By No. 200 sieve	97.66	97.72	-	-
By No. 325 sieve	-	-	88.5	-

students and others and proved to be the most recommendable percentage for the substitution of fly ash for Portland cement. Also two-inch diameter by four-inch height cylinders were made with some of the fly ashes on which the research was conducted. Control specimens were prepared each day that specimens containing fly ash were made. All cement-fly ash combinations were repeated with each of four cements and some were repeated with six cements. The properties of some of the cements used have been shown in Table 2.

The tests of the mortars were performed in accordance with the test for Compressive Strength of Hydraulic Cement Mortars, A. S. T. M. Designation C109-54T, except for the mixing which was done according to the method of "Mechanical Mixing of Hydraulic Cement Mortars of Plastic Consistency; A. S. T. M. Designation C305-55T" in order to assure uniformity of the mortars. The machine used in compressive strength tests is shown in Plate I. As specified in the above mentioned A. S. T. M. procedures, a uniform consistency of all mortars was maintained by adjusting the amount of water added to each mix according to the table flow test required in A. S. T. M. C109-54T. The effect of each particular fly ash on the amount of mixing water required is indicated by the "water requirement ratios" shown on the curves in Figs. 1 through 5. This percentage ratio is calculated by dividing the amount of water required by the cement-fly ash mortar by that required by the control mortar and multiplying by 100. By comparing these water requirement ratios as shown on the graphs it becomes clear that fly ashes with moderate amounts of sulfur trioxide, about

EXPLANATION OF PLATE I

Compression testing machine with cylindrical specimen.

PLATE I



5.0 percent or less, do decrease the water requirement of the mortar, but those with high percentages of sulfur trioxide, such as the Ridgeland and the BLR3-H5 fly ashes do actually increase the water requirement of the mortar.

After removal from the molds at the age of 24-hours, all specimens were stored in water in the air conditioned laboratory of the Kansas Highway Commission at Kansas State College. The temperature was always maintained at about 73° F. until specimens were tested at 7, 28 and 90 days for compressive strength. Every value on the curve is an average of three specimens made of the same mix, stored together and tested at the same time.

Examining the curves in Figs. 1 through 5 one sees that different cements have resulted in different compressive strength curves while the corresponding cement-fly ash curves took somewhat the same trend as their particular cement control curves. From these curves it can safely be concluded that cement-fly ash mortars possess less compressive strength at early ages (7 to 28 days) than mortars made of cement alone. This reduction in early strength is due to the fact that at this age not enough pozzolanic action had taken place to compensate for the reduction in strength caused by the use of less cement. However, this decrease in strength at early ages is not great as compared with the increase in strength at later ages.

The influence of high sulfur trioxide content on the compressive strength of the mortar is to increase it even at early ages. This fact was demonstrated by the Ridgeland fly ash which produced higher strength than the control specimens although its mortar had

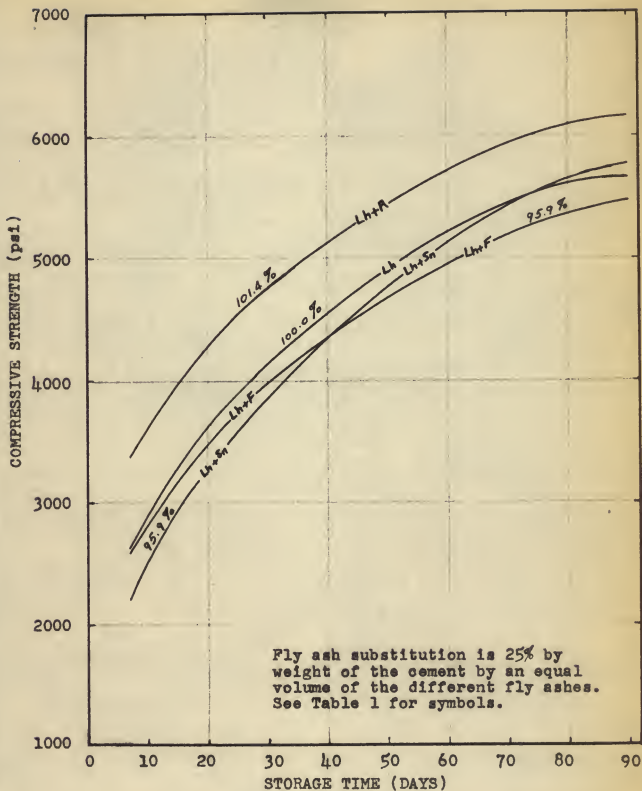


Fig. 1. Compressive strength diagrams for Lehigh cement-fly ash mortar cubes.

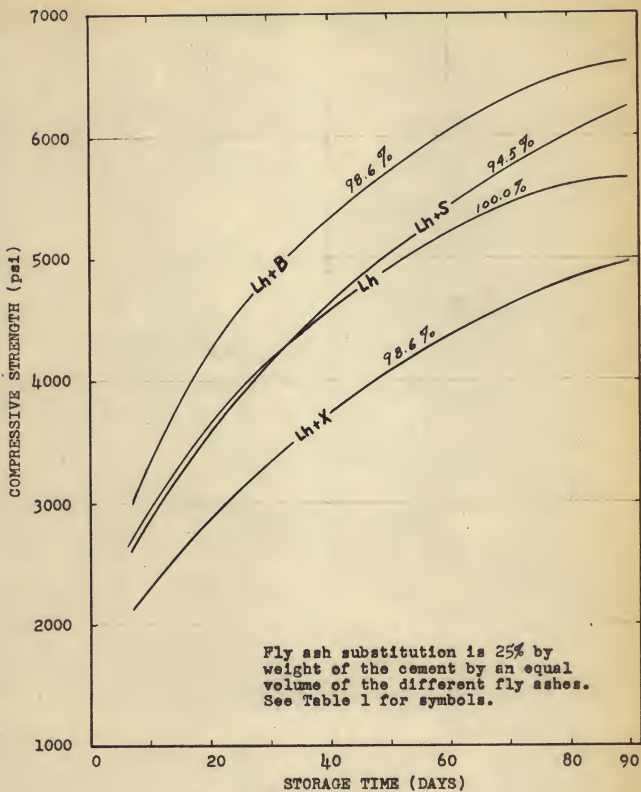


Fig. 2. Compressive strength diagrams for Lehigh cement-fly ash mortar cubes.

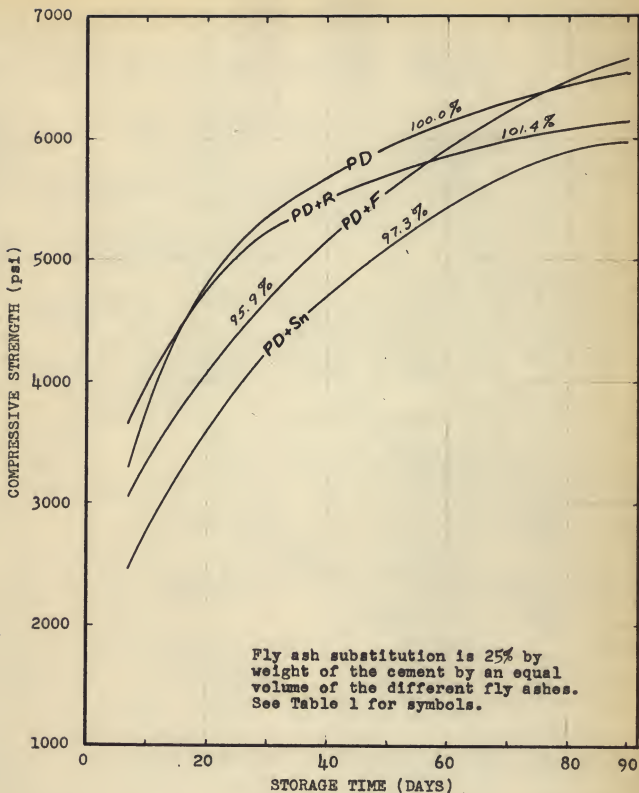


Fig. 3. Compressive strength diagrams for Penn Dixie cement-fly ash mortar cubes.

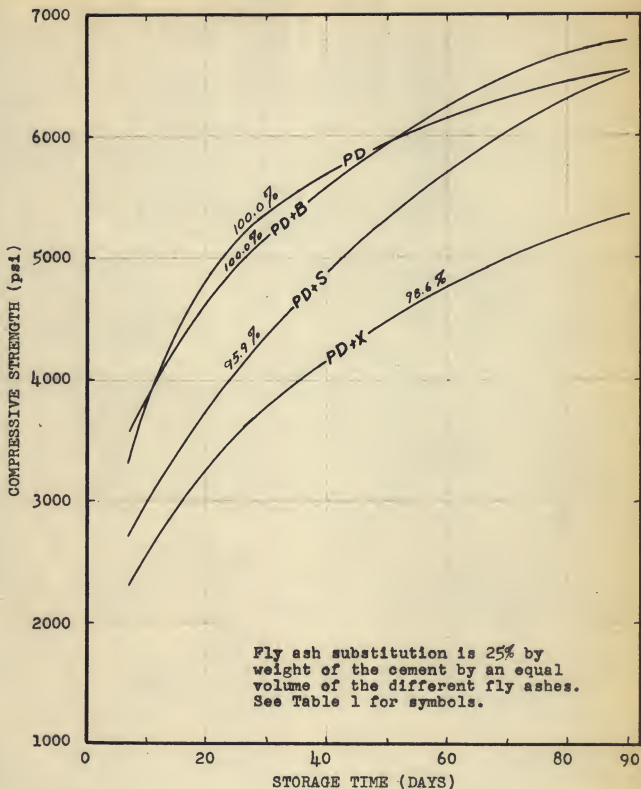


Fig. 4. Compressive strength diagrams for Penn Dixie cement-fly ash mortar cubes.

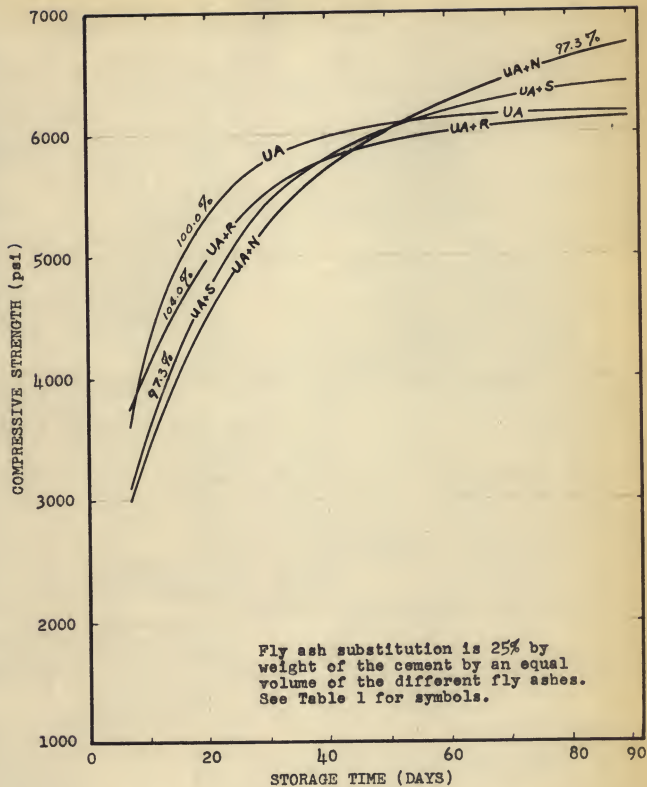


Fig. 5. Compressive strength diagrams for Universal Atlas cement-fly ash mortar cubes.

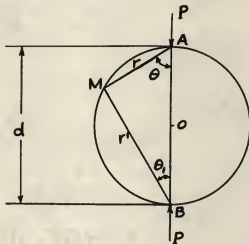
a high "water requirement ratio" which usually results in a weaker mortar than that requiring less mixing water.

By looking at the different curves in the Figs. 1 through 5 one cannot actually pick one fly ash as the best strength developing except for the Ridgeland with the high SO_3 content. From the others the Fisk fly ash with 4.08 percent gives the most consistent results.

By comparing the results of the two-inch cubes with those of the two-inch diameter by four-inch height cylinders it was clear that the cylinders' tests show more pronounced decrease in early compressive strength than do tests of the two-inch cubes. This decrease in strength of test cylinders over test cubes could be attributed to a combination of axial stresses together with probable bending stresses on the four-inch long cylinders as compared with mere axial stresses on the short two-inch cubes. This difference has lead to the development of the tensile splitting tests in which compressive as well as tensile stresses are calculated on the same specimen. This test was developed independently in Japan by Akazawa and in Brazil by Carneire.

The tensile splitting test is performed on cylindrical specimens loaded to failure in the direction of its diameter. Experiments made in Denmark and Norway indicated that the tensile splitting strength is largely independent of length and diameter of the specimen tested. Although this test is in its preliminary stages of development and is not yet adopted, the fairly proved advantages indicate its feasibility for the future. Cylindrical specimens and compressive strength testing machines can be used for the

determination of both tensile strength and compressive strength. The tensile splitting strength thus calculated is closer to the true tensile strength than the flexural strength found by the 6 x 6 inch beam of 18-inch span broken by bending. It is also easier and less expensive to core a cylindrical specimen from hardened concrete than to cut out a beam and a cube. The tensile splitting test is thought to be less sensitive to small cracks occurring in the exterior of the specimen than the beam test, because the exterior parts of the cylindrical specimen are always in compression. This is proved as follows by Timoshenko on a circular disk loaded with two equal and opposite forces "P" acting along the diameter AB. Assuming that each of the forces produces a simple radial stress distribution equal to: $R = \frac{2P}{\pi} \frac{\cos \theta}{r}$



The forces to be applied on the circumference of the disk to maintain the above stress distribution can be obtained as follows: At "M" of the circumference, we have compression in the direction of $r = \frac{2P}{\pi} \frac{\cos \theta}{r}$ and in the direction of $r' = \frac{2P}{\pi} \frac{\cos \theta_1}{r'}$. Since r and r' are perpendicular to each other and since, $\frac{\cos \theta}{r} = \frac{\cos \theta_1}{r'} = \frac{1}{d}$

we conclude that the two principal stresses at "M" are two equal compressive stresses of magnitude of $\frac{2P}{\pi d}$ each. Hence the same compressive stress is acting on any plane through "M" perpendicular to the plane of the disk, and normal compressive forces of the constant intensity $\frac{2P}{\pi d}$ should be applied to the circumference of the disk in order to maintain the assumed pair of simple radial stress distribution.

Tensile Strength

Mortar briquettes were made of a 1:2.75 cement-aggregate mortar for the control specimens. For the cement-fly ash mortar 25 percent by weight of the cement was replaced by an equal volume of different fly ashes. Mixing, molding and testing were performed according to the standard method of test for "Tensile Strength of Hydraulic Cement Mortars," A. S. T. M. Designation C190-49.

Under conditions of continuous moist curing in the air conditioned Kansas Highway Commission Laboratory of 73° F. temperature, the tensile strength at early ages were a little less or about the same for mortars containing fly ash as for corresponding mortars containing straight Portland cement. However, at the later ages (28 days or more), under these conditions of curing the tensile strength was about the same and sometimes higher for cement-fly ash mortars than for cement alone. It has been proved through research that tensile strength continues to increase with the increase in the percentage of fly ash substitution up to 50 percent substitution. Also, under continuous moist curing, mortars containing fly ash do not exhibit that retrogression in tensile

strength at the later ages which is commonly observed in mortars containing straight Portland cement. It is estimated that cement-fly ash mortars acquire their ultimate tensile strength in about one year. Fly ash mortars hold somewhat as good in drying conditions as in moist curing although the other pozzolans show decrease in tensile strength on drying.

As for the test itself as outlined by A. S. T. M. Designation C190-49, it seems to be inadequate because it cannot be performed except on especially made briquettes. Also the beam bending test is not adequate because it is affected greatly by the cracks in the cored concrete specimen. Therefore, as has been explained in the article on compressive strength the "tensile splitting test" seems to be the most adequate.

As for the effect of the amount of sulfur trioxide present in the fly ash the test specimens did not show much difference in tensile strength from one fly ash with high SO_3 content to one with low SO_3 content. Therefore, it could be concluded that the sulfur trioxide influence on the tensile strength is negligible.

Alkali-Aggregate Reaction and Expansion

A frequent cause of failure in concrete is the expansion and the consequent cracking resulting from the alkali-aggregate reaction. This reaction was described first by Stanton in 1940 as one between the sodium and potassium hydroxides, released by the cement, and a reactive form of silica in the aggregates. Since then many cases of expansion and cracking of concrete have been attributed to the same cause. The reaction leads to the formation

of an alkali silicate gel and sets up expansive forces in the concrete. The action is a relatively slow one taking a year or more to show signs of distress in the concrete. Those signs are manifested first by expansion without cracking but being evidenced by the closing of expansion joints, or displacement of kerbs in roads, or the misalignment of different parts of a structure. This is followed by random pattern cracking and in some cases by the exudation through cracks and pores of a soft viscous gel which, on exposure hardens and turns whitish.

For the above reaction to occur, however, both a relatively high content of alkali in the cement and the presence of particular reactive constituents in the aggregate are necessary. Thus no alkali reaction takes place when high alkali cements are used with inert aggregates, or when reactive aggregates are used with cements of low alkali content. But since neither case may exist except rarely and only in the laboratory, alkali-aggregate reaction is usually expected. The content of alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) in cements may be as low as 0.10 percent which is the value for the Penn Dixie (PD) cement or may rise above 1.0 percent as shown by the Universal Atlas (UA) cement which has a value of 1.12 percent as shown in Table 2. A substantial proportion of these alkalis passes into solution in water quickly. The total alkali (symbolized by R_2O) is usually calculated as equivalent Na_2O . This is the percentage content of Na_2O plus 0.658 times the percentage content of K_2O although there is some uncertainty whether at equivalent concentrations KOH and NaOH are equal in their effect. Cements with an (R_2O) content below 0.6 percent have been found,

as a rule, to cause little expansion with reactive aggregates, but there are exceptions. Such cements are commonly called "low-alkali" cements. Occasionally an aggregate itself may contain soluble alkali salts, or, as in the case of zeolite, produce them by base exchange.

The mechanism of expansion caused by the alkali-aggregate reaction is not yet entirely solved. The simplest theory ascribes it to the direct enlargement of the affected pieces of aggregate producing pressures which rupture the concrete just as hydration of hard burnt lime or magnesia produces unsoundness in the cement. Other theories concentrate attention more on the properties of the reaction product than on the immediate growth of aggregate particles. The gels formed as reaction products are alkali silicates containing a certain amount of lime. One theory ascribes the expansive pressure to the absorption of water by the gel as long as it remains sufficiently rigid to exert a uni-directional pressure. Another theory acceptable to some people describe the expansive pressure as an osmotic pressure. In this theory the hardened cement paste around the reactive particle is assumed to act as a semi-permeable membrane allowing alkali hydroxide to diffuse through to the particle, but preventing the complex silicate ions produced by the alkali-aggregate reaction from passing out. Thus the reaction product itself may react with the cement at the walls of pores to form a semi-permeable membrane which may consist of an alkali calcium silicate which is more dense than the original reaction product. According to Lea and Desch in The Chemistry of Cement and Concrete, concrete and mortar have been shown to act

as semi-permeable membranes to water-glass solutions and pressures of over 500 p.s.i. developed.

According to Lea and Desch (7) there is a certain content, known as the "pessimum" content of reactive material in an aggregate that leads to maximum expansion. This "pessimum" content may be as low as 3.0 to 5.0 percent in the case of opal, whereas with less active materials it may be 10.0 to 20.0 percent, or even rise to 100 percent. With very active materials the maximum expansion of a concrete tends to increase with the particle size, but with less active materials the reverse is true. Very finely divided materials (cement fineness) may in either case cause no expansion. Less effect on expansion is also found with porous aggregates and concretes, in which space is available to accommodate the reaction products, than in dense concrete. The degree of reaction and the degree of expansion are not synonymous terms since some reactions have corrective effects on the expansion. The expansive effect is probably related to the ratio of alkali to reactive silica, which determines the amount of alkali available to each reactive particle, and the relative local concentration of alkali and lime since the latter appears to reduce the tendency of the reaction product to form a swelling gel. Too small amounts of alkali can cause little gel formation while too large amounts produce a fluid reaction product less capable of exerting pressures. Water is also essential to the expansion which does not occur in dry concrete.

It has been found through research that the destructive effect of the alkali-aggregate reaction could be prevented or reduced

somewhat by the use of pozzolans. Although no alkali-aggregate reactions could have occurred in the mortar bars of this research because of the use of the inert graded Ottawa sand as the aggregate, expansion due to some other constituents such as sulfur trioxide have taken place. The effectiveness of twelve fly ashes in preventing or reducing this expansion was determined by measuring the change in length of 1-by 1-by $11\frac{1}{4}$ -inch mortar bar specimens made of mortar of 1:2.25 ratio of cement to aggregate in which 25 percent by weight of the cement was replaced by an equal solid volume of the twelve different fly ashes. Six different cements from which four are analyzed in Table 1 were used. In all other respects the procedure outlined in the test for "Shrinkage and Expansion of Mortar; A. S. T. M. Designation C227-52T" was followed. The measuring instrument used is the "length comparator" shown in Plate II. This instrument is accurate to one ten thousands of an inch.

By checking the Figs. 6, 6a, 7, 7a, 8, 8a, 9 and 9a for the expansion it becomes clear that the two fly ashes (Ridgeland R and BLR3;H5 B) with the high sulfur trioxide content are the only two with pronounced increase in expansion over the cement control specimens. All the other fly ashes had an equal or less expansion than the control specimens over the 28 days in which the specimens were stored in water at constant temperature of about 73° F.

The mechanism of the action of fly ash in particular and of pozzolans in general in reducing expansion is not clear, but there is an idea that it is related to their ability to take up sodium or potassium from solution. This may result in distributing the

EXPLANATION OF PLATE II

Length comparator for measuring the change in length of bars.

PLATE II



reaction product throughout the concrete, rather than in localized masses around aggregate particles capable of producing osmotic or swelling pressures. The composition of the gel formed, and its properties, may also be changed.

Contraction

The influence of fly ash in particular or of pozzolans in general on the contraction of Portland cement mortars or concretes is more pronounced than their effects on expansion. This fact is well demonstrated throughout the bar diagrams in Figs. 6 through 14a. This data was obtained on the same bars used for expansion. These bars were taken out of the water after 28 days and stored in special boxes in the air conditioned Kansas State Highway Commission laboratory at about 73° F. The boxes were designed specially to hold the bars in vertical position while resting on their bases and not their pins. This vertical storage gave better results by doing away with the errors due to the deflections of horizontally stored bars.

The examination of the bar diagrams for contraction points out the fact that cement-fly ash mortar bars acquire the major amount of their shrinkage during the first 28 days of dry storage after which the shrinkage continues on a small decreasing scale to about a year. Although pozzolanic activity continues for a period of about five years the shrinkage is negligible after the first year.

Looking over Figs. 6 and 6a it is seen that the Fisk (F) fly ash with 4.08 percent SO_3 and the Northwestern (N) fly ash with

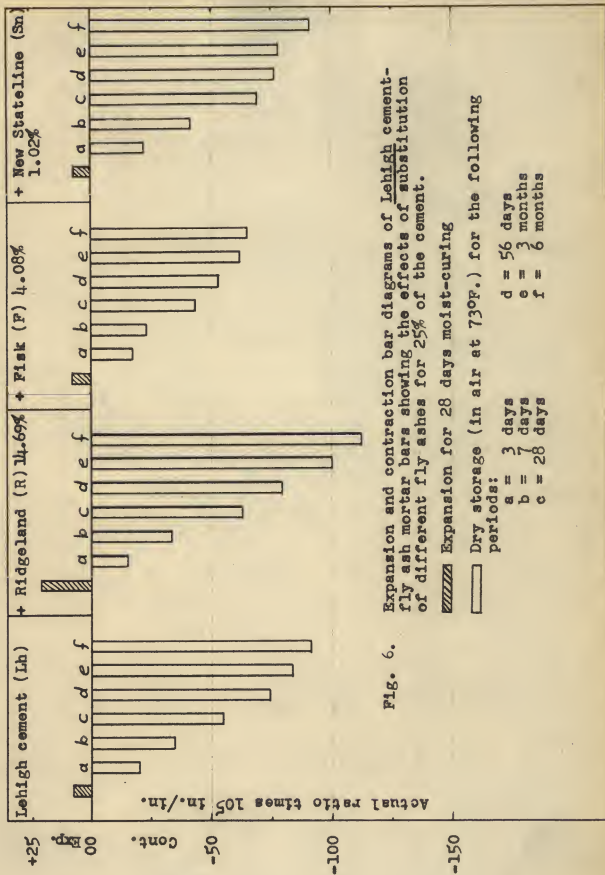


Fig. 6. Expansion and contraction bar diagrams of Lehigh cement-fly ash mortar bars showing the effects of substitution of different fly ashes for 25% of the cement.

Expansion for 28 days moist-curing

Dry storage (in air at 73°F.) for the following

periods:

a = 3 days

b = 7 days

c = 28 days

d = 56 days

e = 3 months

f = 6 months

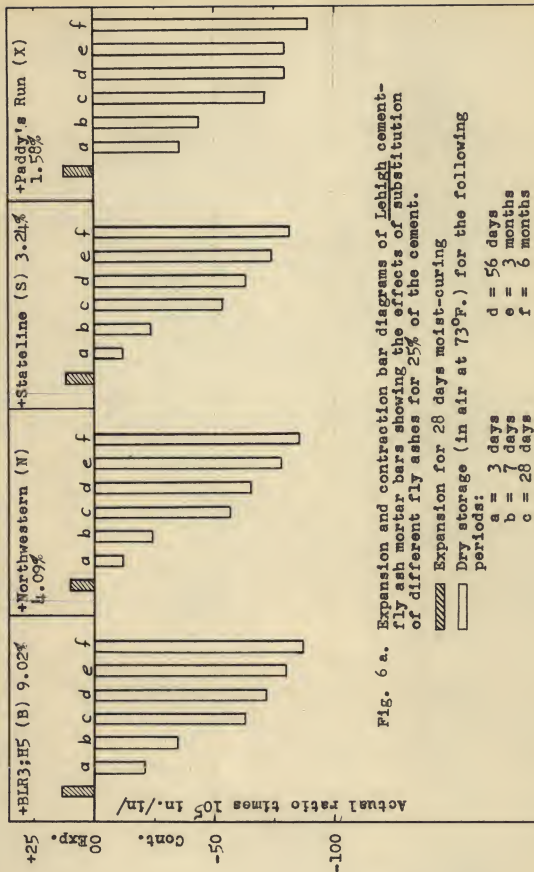


Fig. 6 a. Expansion and contraction bar diagrams of Lehigh cement-fly ash mortar bars showing the effects of substitution of different fly ashes for 25% of the cement.

Expansion for 28 days moist-curing

Dry storage (in air at 73°F.) for the following periods:

a = 3 days

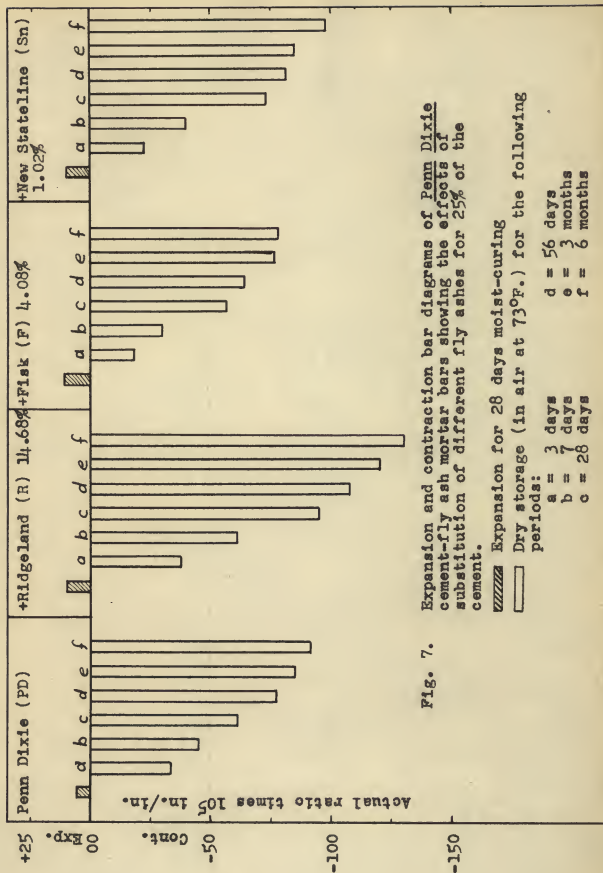
b = 7 days

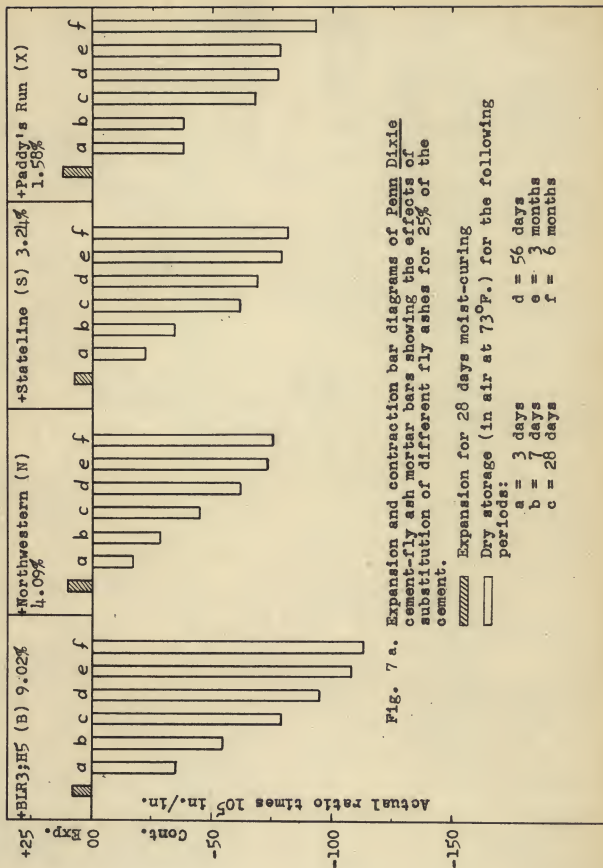
c = 28 days

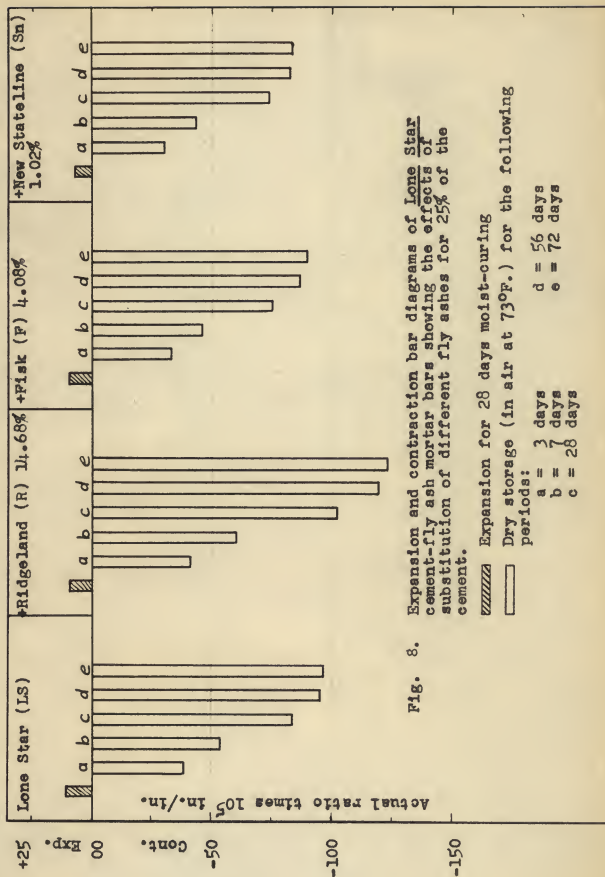
d = 56 days

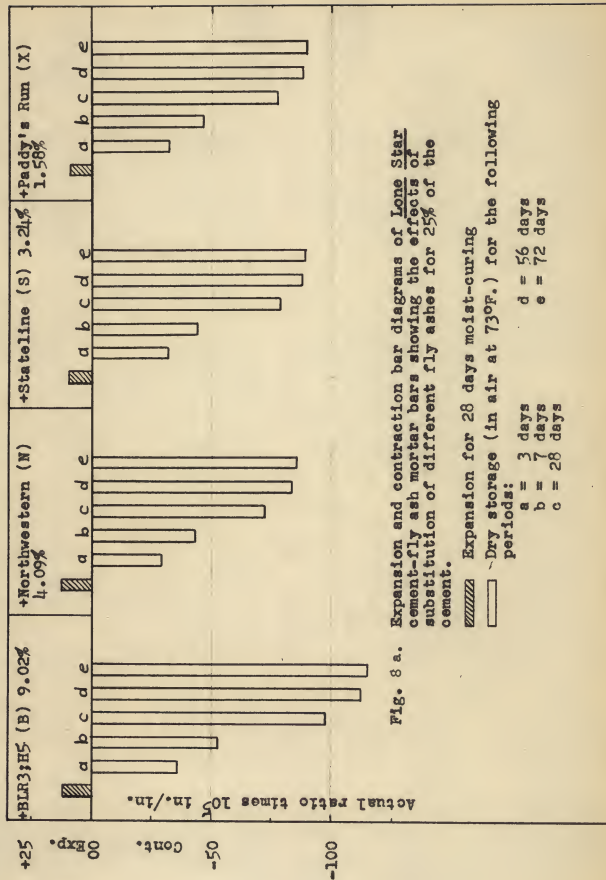
e = 3 months

f = 6 months









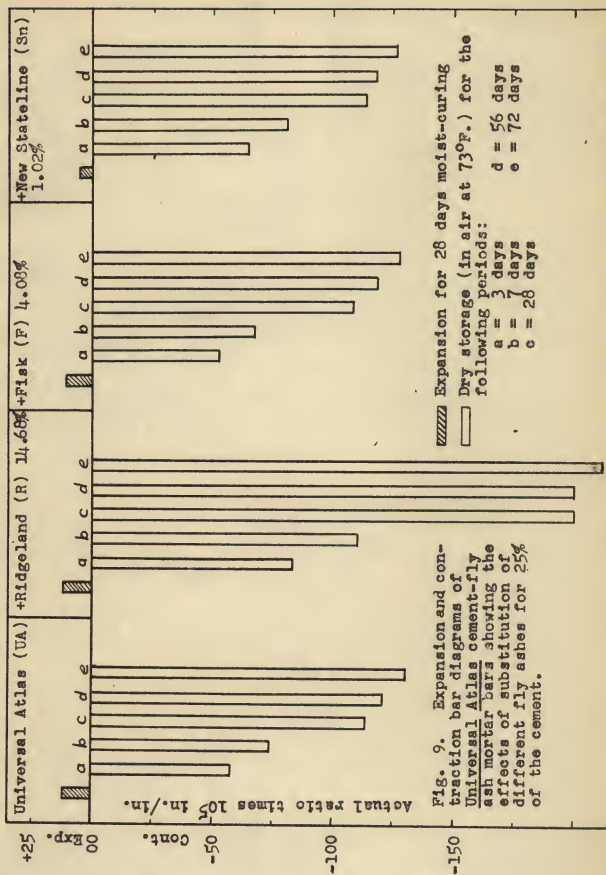
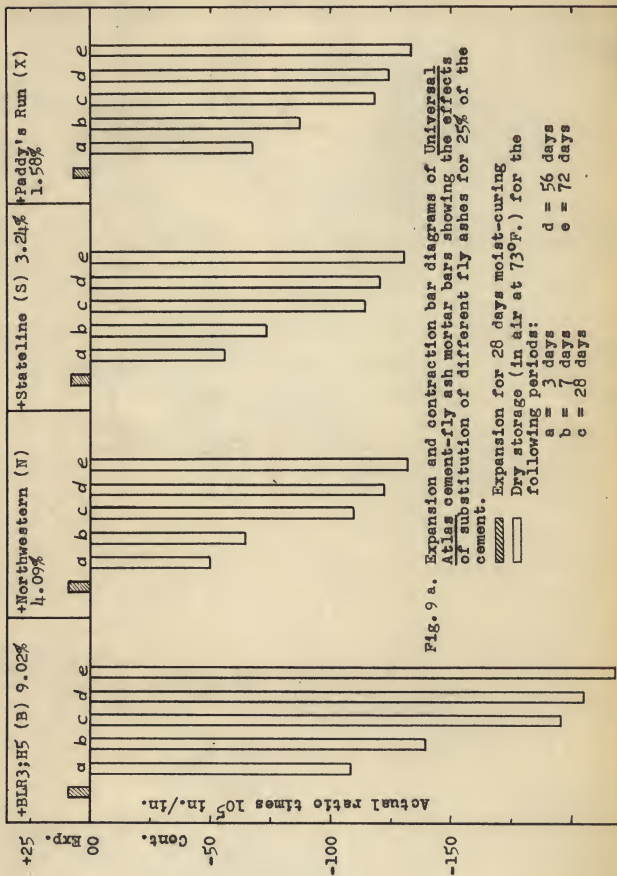


Fig. 9. Expansion and contraction bar diagrams of Universal Atlas cement-fly ash mortar bars showing the effects of substitution of different fly ashes for 25% of the cement.

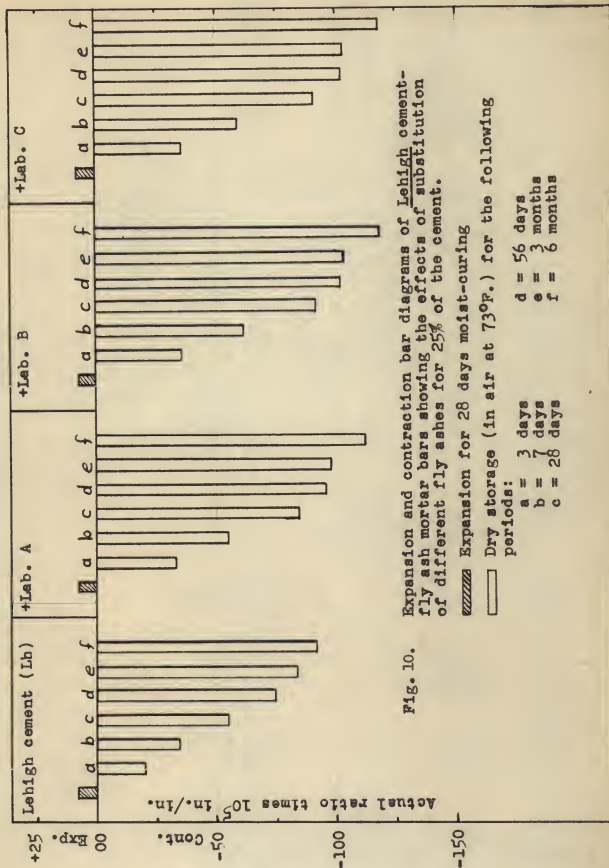


4.09 percent SO_3 have exhibited the best shrinkage values over the six months period of the tests. Those two fly ashes actually resulted in less shrinkage than did the Portland cement control specimens. This is well clear in Figs. 6 and 6a. It is also seen that fly ashes, such as the New Stateline (Sn), with the lowest sulfur trioxide content (1.02%) as well as the fly ashes with the highest sulfur trioxide content, such as the Ridgeland (R) fly ash, did increase the shrinkage values over those of the control specimens. Throughout Figs. 6, 6a, 7, 7a, 8, 8a, 9 and 9a the Fisk (F) and Northwestern (N) fly ashes with sulfur trioxide content of 4.08 percent and 4.09 percent successively gave the best results and did actually reduce the shrinkage of the mortar bars.

From the results of this research as shown in Figs. 6, 6a, 7, 7a, 8, 8a, 9 and 9a it is to be concluded that the limits of sulfur trioxide in fly ash for the most desirable results should be specified between four percent and six percent with the five percent limit as the most desirable and sought for.

As for the influence of the cements themselves on the shrinkage, Figs. 6, 7, 8, 9, 10, 11, 12, 13 and 14 show that only the Universal Atlas (UA) cement resulted in shrinkage well above the 0.00100 in./in., while the others were well below this value. This is mainly due to the high alkali content (R_2O) of the cement as shown in Table 2. The sulfur trioxide contents of all the cements used were within the three percent maximum allowed for cements.

Although no chemical analyses have been obtained for the fly ashes designated as Lab. A, Lab. B, Lab. C, Lab. D and Lab. E,



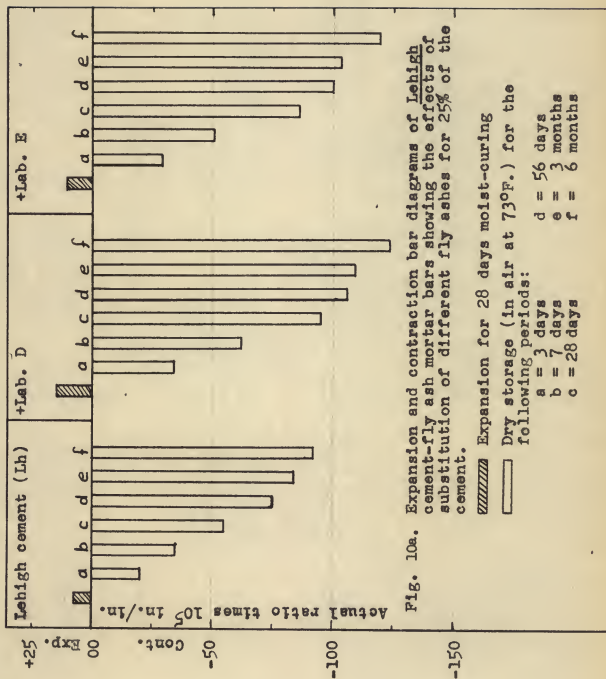
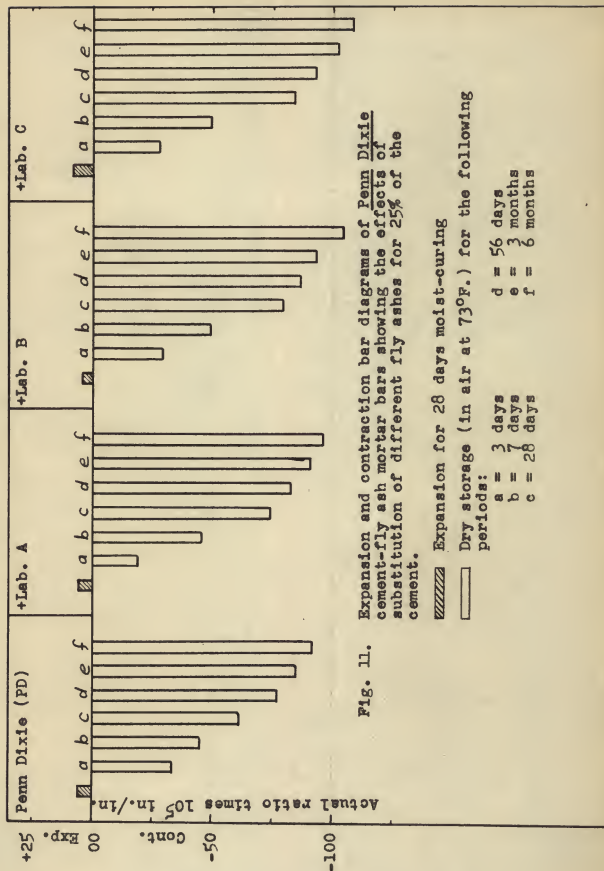
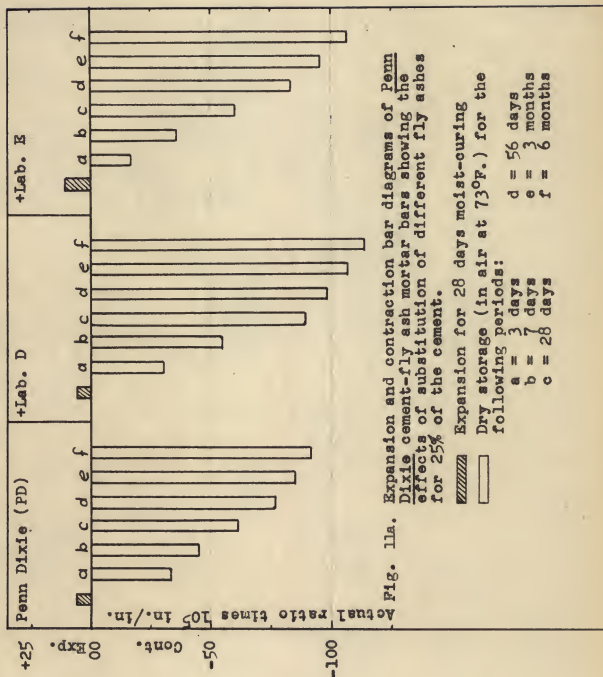
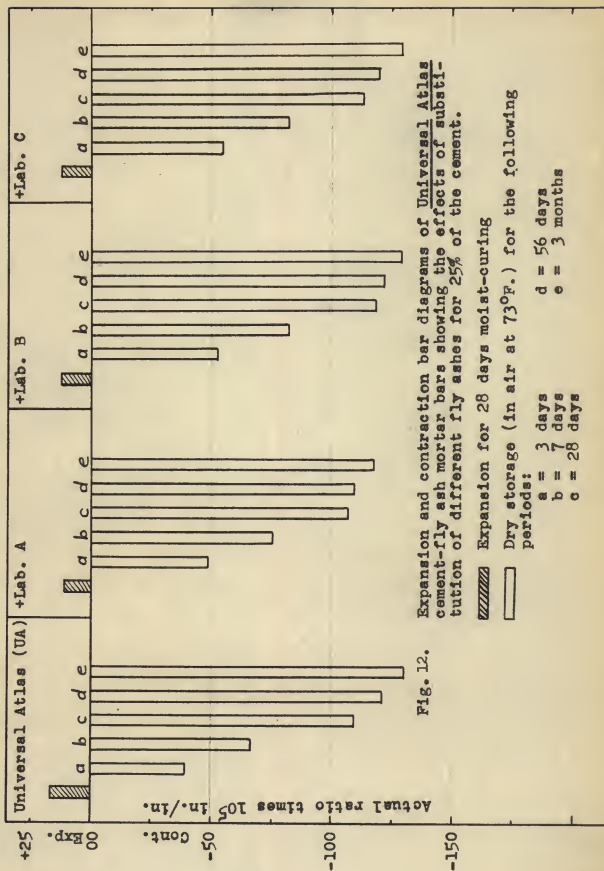
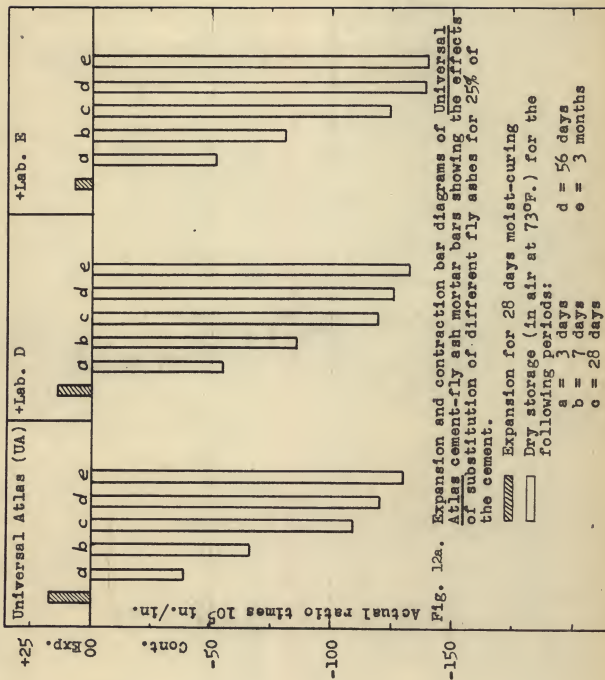


Fig. 10a. Expansion and contraction bar diagrams of Lehigh cement-fly ash mortar bars showing the effects of substitution of different fly ashes for 25% of the cement.









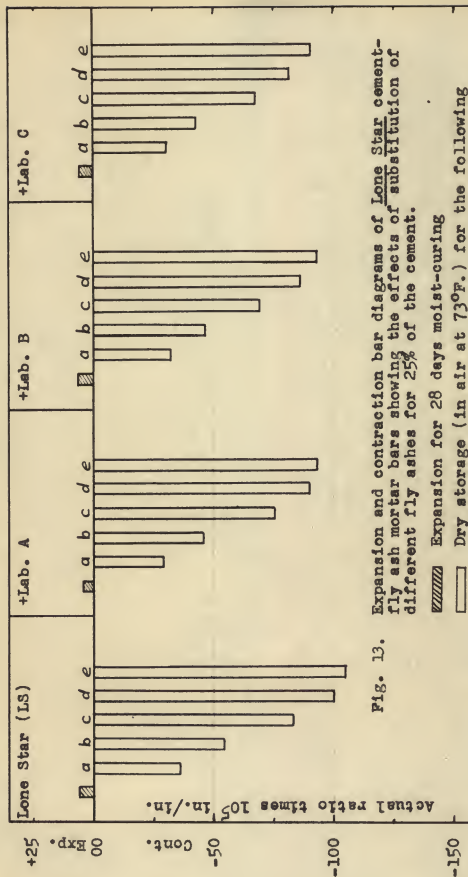
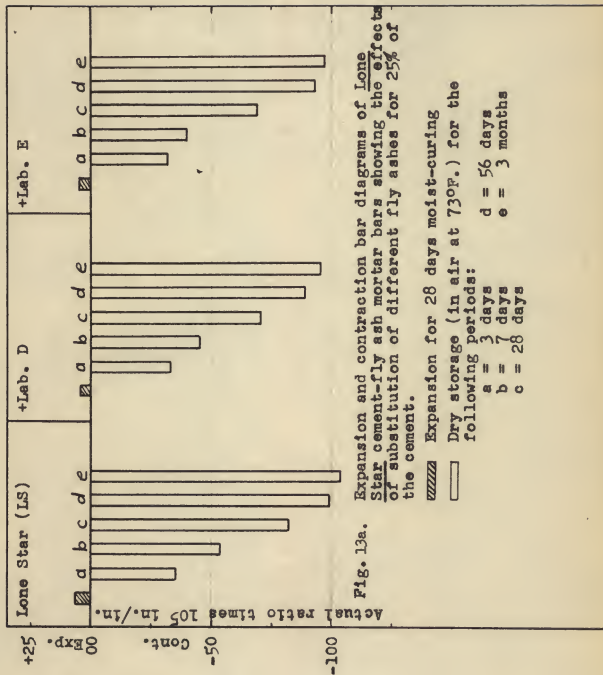


Fig. 13. Expansion and contraction bar diagrams of Lone Star cement-fly ash mortar bars showing the effects of substitution of different fly ashes for 25% of the cement.

Expansion for 28 days moist-curing

Dry storage (in air at 73°F.) for the following periods:

a = 3 days
b = 7 days
c = 28 days
d = 56 days
e = 3 months



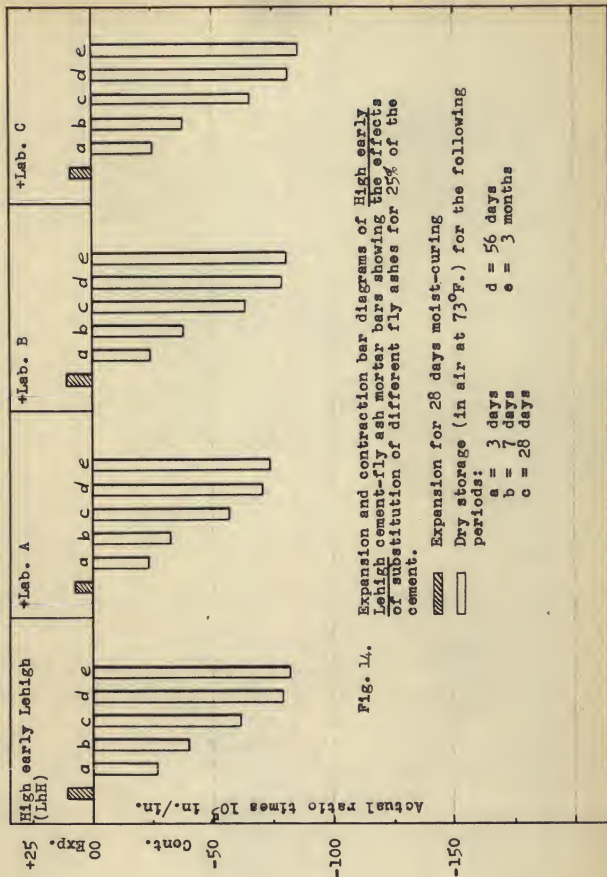
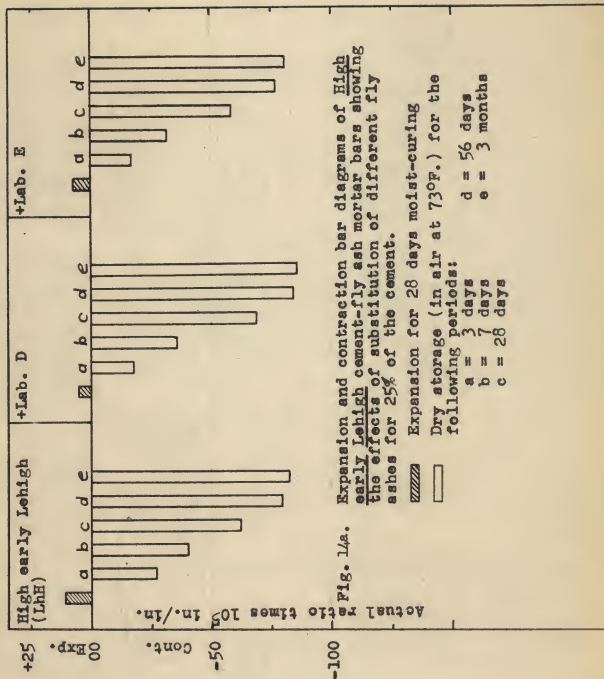


Fig. 14. Expansion and contraction bar diagrams of High early Lehigh cement-fly ash mortar bars showing the effects of substitution of different fly ashes for 25% of the cement.



the tests results as shown in Figs. 10, 10a, 11, 11a, 12, 12a, 13, 13a, 14 and 14a indicate that the sulfur trioxide content of the fly ashes did not differ much from one another and that they probably are within the four percent to six percent limits recommended above. Although there was only very little reduction in shrinkage due to the use of these particular fly ashes, they are to be recommended for use if available due to economic considerations and to the fact that they will not produce any harmful effect on the concrete but will definitely result in desirable qualities of concrete such as better workability, less permeability, and less water requirement ratios.

TEMPERATURE EFFECTS ON CEMENT-FLY ASH MIXES

Previous investigations on pozzolans proved that the rate of reaction and strength development of pozzolana-lime mixes increased with rise in temperature. This fact was reflected, in this research, in the behavior of the cement-fly ash mortars such as the Ridgeland (R) fly ash which produced a tremendous amount of heat as demonstrated by the heat-of-wetting test. This test was conducted on some of the fly ashes used. In this test a thermos bottle was used in which 50 grams of the fly ash were put. Fifteen to twenty milliliters of distilled water were poured over the fly ash through a funnel fixed into a stopper through which a thermometer reached the fly ash. The temperature rise was measured.

In the mortars for the compressive strength cubes this temperature rise produced by Ridgeland (R) fly ash contributed to the early strength in the first few hours by accelerating the

rate of hydration. Further, since SO_3 tends to increase early strength development, the one-day strength as indicated by the curves on Figs. 1, 3 and 5 shows unusually high one-day strength. Also, the BLR3;H5 (B) fly ash, which was second in heat generation in the heat-of-wetting tests, resulted in accelerating the development of the first few hours or one day compressive strength as shown by Figs. 2 and 4.

The rate of strength development, according to Lea and Desch (7) is so marked that a pozzolan which is comparatively inert for weeks at the average temperatures prevailing in the United States of America, and therefore of relatively little value, may prove satisfactory under the temperatures attained in the Mediterranean summer and in more tropical climates. It is worth noticing, though, that at lower temperatures the rate of strength development of pozzolanic cements is affected more adversely than that of Portland cements alone.

ECONOMIC ASPECTS

Natural Pozzolans

There are many geologic formations throughout the United States of America which are known to yield suitable pozzolanic materials. These formations occur in stratified deposits which vary greatly in composition, texture, degree of consolidation and other properties. These pozzolans require grinding to one degree or another and some require drying. These requirements affect the cost of production which is also affected by the nature of the

source of the pozzolan, the character of the raw material, and the conditions affecting development and exploitation. Where mining is required the cost is higher than for open excavation. The overburden, the geographical location, roads, and railroads are important factors in cost.

Fly Ash

In regions where powdered coal-burning power plants and steel mills are prevalent, fly ash and slags are used as the source for pozzolans. For the fly ashes to have the chemical constituents and the physical properties needed to make them suitable as pozzolans for use in concrete the burning of the coal should be controlled. This control requirement affects the cost of the fly ash but the necessity of getting rid of this by-product justifies the extra cost of burning control.

The need for good well protected storage of fly ash is a factor of cost. Fly ashes if not carefully stored will absorb moisture from the air and cause bleeding of the concrete when used in it.

USES OF FLY ASH

Fly ash due to its pozzolanic property is used in concrete in order to produce more desirable qualities such as better workability, less permeability, higher tensile strength, reduction in the heat of hydration and temperature, increased resistance to sulfate attack, higher compressive strength at later ages, and reduced alkali-aggregate reaction and the consequent expansion.

It has been used most extensively in mass concrete, particularly large dams, where many of the changes it produces in concrete are of value. Since fly ash is less expensive than Portland cement, the replacement of part of the latter with fly ash produced significant savings in the cost of certain big projects such as the Hungry Horse Dam on the Flathead River in western Montana.

Fly ashes are to be used for the most pozzolanic benefits in hot or tropical regions where high temperatures accelerate pozzolanic activity resulting in more desirable concrete properties.

CONCLUSION

Due to its pozzolanic properties fly ash produces more desirable quality concrete when substituted for a portion of the Portland cement required in the mix.

The compressive strength of cement-fly ash mortar cubes is influenced by the amount of sulfur trioxide present in the fly ash. The early strength of mortars seems to be equal or higher when fly ashes with high sulfur trioxide (8% or above) content are used than when Portland cement alone is used. But for fly ashes with medium sulfur trioxide (3.5% - 7.5%) content the early compressive strength is either equal or a little less than that of Portland cement alone. As for fly ashes with low sulfur trioxide content (below 3.5%) the early compressive strength is definitely lower than that of Portland cement alone. At later ages (above 28 days) all fly ashes with pozzolanic properties produced compressive strengths either equal to or greater than those of Portland cement alone.

The tensile strength of cement-fly ash mortars is usually equal to or greater than that of Portland cement mortars at early ages (up to 28 days). But at later ages the tensile strength for cement-fly ash mortars is definitely higher than that of Portland cement mortars.

Due to differences in compressive strength results when two-inch cubic specimens are used as compared with cylindrical specimens of two-inch diameter by four-inch height, it is to be concluded that the tensile splitting test might give more consistent and helpful results for both compressive and tensile strengths.

According to the test results of this research it is to be concluded that fly ashes with high SO_3 content (above eight percent) do increase the expansion and the contraction of mortar bars and are therefore not suitable. But the limits of SO_3 content in fly ash to be recommended are from four percent to six percent with the five percent limit as the most desirable and sought for.

ACKNOWLEDGMENT

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THE USE OF FLY ASH AS A POZZOLANIC MATERIAL IN
PORTLAND CEMENT CONCRETE

by

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Fly ash is a powdery residue of roughly spherical shape particles solidified from the ashes of burnt pulverized coal. This residue is collected, in modern power plants, at the entrance of the stack by electrical or mechanical precipitators in order to prevent pollution of the air. Due to its pozzolanic properties fly ash is used in the concrete either as an addition or as a substitution to a part of the cement required in the mix. Pozzolans are usually defined as siliceous or siliceous and aluminous materials, which in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. This calcium hydroxide is usually the product of hydration of Portland cement.

The objective of this research was to study the pozzolanic behavior of fly ash as shown by its effect on Portland cement-fly ash mortars. The results were to be used by the Chicago Fly Ash Co. for the production of better fly ashes by controlling the burning process, and by the experiment station for recommendations on the establishment of suitable specifications for the use of fly ash. The limits for the sulfur trioxide (SO_3) content in the fly ash were the focal point of study in this research.

Twelve different fly ashes were used together with six different cements. Chemical analyses and physical properties of most of the cements and fly ashes were obtained and studied. The sulfur trioxide content of the fly ashes were reported. Graded

Ottawa sand was used throughout the experiments thus asserting the absence of alkali-aggregate reactions.

The compressive strength tests were performed on two-inch cubes and on cylinders two-inches in diameter by four-inches in length. Mixes of 1:2.75 ratio of cement to aggregate were used with 25 percent by weight of the cement replaced by an equivalent volume of the different fly ashes. The amount of water used was determined by the table flow test. Fly ashes with high SO_3 content (above eight percent) increased the early age compressive strength, while fly ashes with medium SO_3 content (3.5% - 7.5%) gave an equal or higher early compressive strength as did the control specimens, and fly ashes with low SO_3 content (below 3.5%) decreased the early compressive strength. All fly ashes produced either equal or higher strength after long periods (above 28 days) of storage.

The tensile strength tests were performed on mortar briquettes of a mix as that of the compressive strength specimens except for the water which was held constant. Early tensile strength was either equal or higher than that of control specimens. No noticeable differences between the different fly ashes were apparent. Accordingly the SO_3 content of fly ash does not affect the tensile strength much.

For the expansion and contraction tests, mortar bars of 1:2.25 ratio of cement to aggregate were used with 25 percent by weight of the cement replaced by an equal volume of the different fly ashes. The water used was determined by the table flow test.

Portland cement control bars as well as cement-fly ash mortar bars were made at the same time. The high SO_3 content fly ashes (above eight percent) increased the 28 days expansion over that of the control specimens. The other fly ashes with less than eight percent SO_3 content produced either the same amount of expansion or less than that of the control specimens.

As for the shrinkage at dry storage, the high SO_3 content fly ashes did increase it considerably while the low SO_3 content (below 3.5%) fly ashes produced a small increase in shrinkage. But the medium SO_3 content fly ashes (3.5% - 7.5%) did actually reduce the shrinkage over that of the control specimens. Therefore, the limits of SO_3 content in fly ash should be from four percent to six percent with five percent limit as the most adequate.